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11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

An important Army research mission is to investigate chemistry leading to better solvent resistant elastomers for military uses as found in face masks, hoses, belts, mounting structures for vehicles, and the like. Our strategy to meet the challenges of this mission begins with creating a base polymer formulation, whereby simple changes in monomer ratio lead to either soft, elastic polymers or hard, tough materials. We have directed our efforts towards solvent resistant materials that improve upon butyl rubber.

Polycarobosilanes combine the hehavioral characteristics of hydrocarbon polymers and siloxane elastomers. We have identified two key structural features in polycarbosilanes that lead to both greater elasticity and higher tear strength. Greater elasticity can be achieved by increasing the run length from just one repeat unit to three repeat units within the soft monomer – the effect is dramatic. Higher tear strength is attained by introducing chain-end latent crosslinking to complement the chain-internal crosslinking – the latter concept, chain-internal latent crosslinking - was defined in earlier work. Chain-end latent crosslinking has enhanced the solvent resistance of these polycarbosilane elastomers.

Interactions with the Army Research Laboratory in Aberdeen, along with Dr. Doug Kiserow of the ARO, have been most helpful.

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REPORT DOCUMENTATION CONTINUATION SHEET: DAAD19-00-1-0160

1. Papers Submitted or Published During Report Period:

a. Manuscripts Submitted, But Not Published:

NATO Advanced Study Institute, Antalia, Turkey, September 2002
"Functionalized Polymers Via ADMET Polymerization", NATO ASI Book Series, In Press, 2003

b. Papers Published in Peer-Reviewed Journals:

A. Cameron Church, Jason A. Smith, James H. Pawlow, and Kenneth B. Wagener, "Non-Traditional Step-Growth Polymerization-ADMET", a chapter in Synthetic Methods and Step-Growth Polymers, Chapter 8, p 431-466. Eds., M. E. Rogers and T. Long, Wiley & Sons, New York, NY (2003).

A. C. Church, J. H. Pawlow, and K. B. Wagener, "ADMET Polymerization as a Route to Functionalized Polycarbosilanes", *Macromolecular Chemistry and Physics*, **204(1)**, 32-39 (2003).

J. C. Sworen, J. H. Pawlow, W. Case, J. Lever, and K. B. Wagener, "Competing Ruthenium Catalyzed Metathesis Condensation and Isomerization of Allylic Olefins", *Journal of Molecular Catalysis*, **194**, 69 (2003).

J. H. Pawlow, A. C. Church, and K. B. Wagener "Synthesis of Functionalized Polycarbosilanes via One-Pot ADMET Polymerization", *Macromolecules*, **35**, 5746 (2002).

E. Melacka, B. Marciniec, Cezary Pietraszuk, A. Church, and K. B. Wagener, "ADMET Copolymerization of Divinyltetraethoxydisiloxane with 1,9-Decadiene Catalyzed by Grubbs' Catalyst", *Journal of Molecular Catalysis*, **190**, 27 (2002).

J. E. Schwendeman, A. C. Church, and K. B. Wagener, "Synthesis and Catalyst Issues with ADMET Polymerization", *Advanced Synthesis and Catalysis*, **344(6+7)**, 597 (2002).

c. Papers Published in Non-Peer-Reviewed Journals or In Conference Proceedings:

American Chemical Society National Meeting, March 2003 (New Orleans)
"Polycarbosilane Elastomers via Chain-Internal and Chain-End Latent Crosslinking"

d. Papers Presented at Meetings, But Not Published in Conference Proceedings:

University of Southern Mississippi, Hattiesburg, MS, April 2002
Symposium Honoring Professor Roger Porter.
"Functionalized and Elastomeric Polymers via Metathesis Chemistry"

2. Scientific Personnel Supported by This Project and Honors/Awards/Degrees Received:

Honors/Awards - K B Wagener
2003 Fellow Induction by the PMSE Division of the American Chemical Society
2003 American Chemical Society Florida Award
2003 Japanese Society for Progression of Science Fellowship

Scientific Personnel Supported
John C. Sworen – 4th Year Graduate Student
Piotr Matlock – 2nd Year Graduate Student
Prof. Fabio Zuluaga - Visiting Scholar, Univ. del Valle

3. Report of Inventions (title only):

"Functionalized Carbosiloxane Materials", US Provis. Pat. Applica. S/No. 60/427,995

4. Scientific Progress and Accomplishments (include significant theoretical or experimental advances):

Our approach to producing solvent resistant elastomers consists of introducing latent reactivity in the polymer backbone. Curing takes advantage of the latent reactive site, which is activated with water at or above room temperature. During this reporting period we have successfully introduced the concepts of Chain-Internal and Chain-end latent crosslinking.

We have done this to enhance the performance of these solvent resistant elastomers, which combine the behavior of carbon-based materials (such as butyl rubber) with silicone soft materials (such as silicone rubber). The goal is to improve upon the elastomer materials used in the military today, such as those found in hoses, facemasks, collapsible water cells and fuel cells, high temperature seals and electronic shielding materials.

Adding chain-end crosslinking to the already-existing chain-internal crosslinking has a significant effect on the overall tensile and tear strength of these hybrid carbon/silicone materials. Our goal now is to amplify and refine this phenomenon, such that latent crosslinking using both chain-end and chain-internal types will produce the strongest possible material.

Second, during this reporting period we enhanced the overall elasticity of these polycarbosilane copolymers by more than 400%. This was done by lengthening the soft phase from just one unit to three units. Important to note is that this was accomplished without a perceptible change in solvent resistance. There is a trade-off here: too long a soft phase will reduce solvent resistance, while too short a soft phase hampers overall elasticity. We are seeking to find the best balance of properties.

These scientific advances have been protected with two patent applications. We will begin presenting these data at the American Chemical Society National Meeting in March, 2003, at the Crosslinking Symposium there. Publications beyond the severn already described in this report are being written to define this new chemistry.

5. Technology Transfer (Any specific interactions or developments which would constitute technology transfer of the research results). Examples include patents, initiation of a start-up company based on research results, interactions with industry/Army R&D Laboratories or transfer of information which might impact the development of products.

We have submitted two patent applications covering the chain-internal and chain-end latent crosslinking concept. The materials that are being created at this point appear to be of sufficient interest to capture the intellectual property that surrounds them.

Materia, Inc, a Caltech startup company specializing in metathesis chemistry, has been contacted as a potential supplier of larger quantities of these polymers. The company desires to commercialize new materials based on metathesis reactions; the latent reactive polycarbosilanes produce by this research are of interest to them. K. B. Wagener, the Principal Investigator for this work, serves on the Scientific Advisory Board of this company.

We have established contact with the Army Research Laboratory to convey the nature of the work being done in our laboratory. Our interests include developing materials for hoses, belts, conformable seals for face masks and EMI shielding of military electronics.